

Cement including composite material, cement products, molding material, a concrete member and a method of producing the same.

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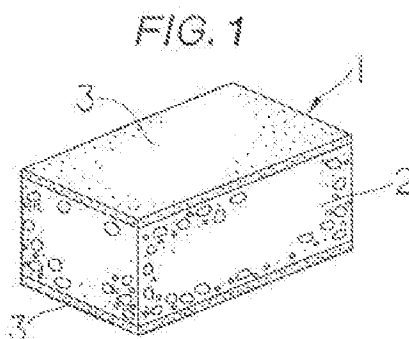
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Abstract of EP 0590948 (A1)

Composite material comprising hydraulic cement and polymer precursor, such as an alcohol-soluble phenol resin precursor which substantially includes no water, but generates water by polymerization. A material with a higher flexural strength and improved water and thermal resistance is thus obtained. Cement products, a molding material and a concrete member (1) are all formed using this material (3).



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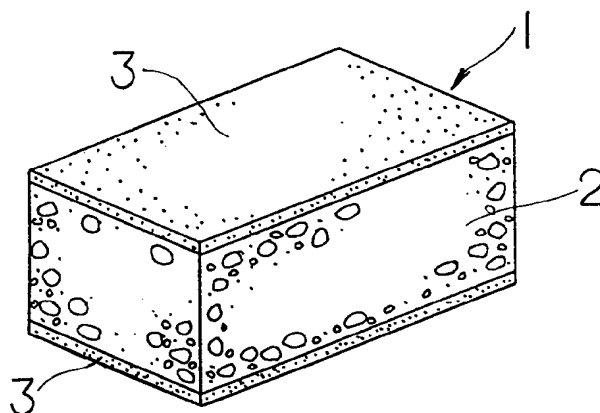
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54 **Cement including composite material, cement products, molding material, a concrete member and a method of producing the same.**

57 Composite material comprising hydraulic cement and polymer precursor, such as an alcohol-soluble phenol resin precursor which substantially includes no water, but generates water by polymerization. A material with a higher flexural strength and improved water and thermal resistance is thus obtained. Cement products, a molding material and a concrete member (1) are all formed using this material (3).

FIG. 1



This invention relates to improvement on cement including composite material, products thereof, and molding material having higher physical strength, more excellent thermal resistance and water resistance and a method for producing them.

5 This invention also relates to improvement on a concrete member having higher physical strength, more excellent thermal resistance and water resistance and a method of producing the same.

There are known various organic or inorganic compounds available for molding materials, adhesives, laminates and other materials used for various fields such as civil engineering and construction industries, transportation industries of cars or railroads, chemical industries, other general mechanical industries and so on.

10 Hydraulic cement has been generally used as mortar or concrete mainly in civil engineering and construction industries while it is combined with more than 25 weight % of water and aggregate is added thereto to produce cement products. The cement products have low flexural strength of 50 to 100 kgf/cm² (5 to 10 N/mm²) although they have high compressive strength and they conventionally have reinforcing bars used therein. In order to improve the flexural strength of the cement products, there are added short glass fibers or carbon fibers thereto. However, their flexural strength rarely exceeds 400 kgf/cm² (40 N/mm²).

15 In general, the cement products have higher physical strength as the amount of water used is lower, and also as the amount of blow-holes included therein is lower.

For example, Japanese Application Publication No. 43431/1984 discloses cement products having extremely higher flexural strength without any fibers included therein and without being molded under high compressive pressure. These cement products can be produced by kneading hydraulic cement, water and water
20 organic polymer with each other while high shearing force is applied thereto by a double roller mill so that sizes and rates of blow-holes in the cement products are limited.

The cement products disclosed in The Japanese Application Publication have higher flexural strength because it is cured by combining hydraulic cement with 7 to 30 % of water relative to hydraulic cement. However, the cement products having flexural strength improved disadvantageously have physical strength lowered when
25 they are immersed in water and also have water resistance lowered due to their swelling when they are immersed in water because of the cement products including water organic polymer.

In order to improve water resistance of the cement products, Japanese Patent Application Laying-Open No. 206342/1988 discloses cement products including isocyanate compound reacted with hydrophilic group of water organic polymer of the aforementioned cement products. Such isocyanate compound may be added
30 to the components of the cement products before they are kneaded or while they are kneaded. Also, they may be impregnated with isocyanate compound after they are kneaded, but before they are cured or after they are cured.

However, such material has bad environment of operations such as kneading and molding because isocyanate compound has strong irritating smell generated therefrom and also has virulence. Furthermore, urethane derivative which is main reactant produced by reacting isocyanate compound with hydrophilic group
35 disadvantageously has lower thermal resistance.

Formaldehyde has been used also for molding materials, adhesives and laminates. Such molding material including formaldehyde is obtained by combining formaldehyde resin precursor with filler such as wood flour, pulp, diatomaceous earth or the like, curing agent, lubricant, coloring agent and/or other additives, grinding
40 and classifying them. In order to lower fragility of such molding material and improve flexural strength thereof, there has been added thereto filler of fibers such as cotton fibers, flax fibers, glass fibers or the like.

Such molding material is molded by compression molding, transfer molding or injection molding to produce mold goods. Such mold goods have flexural strength of 500 to 1000 kgf/cm² (50 to 100 N/mm²) unless there is used filler of fiber material such as glass fibers or flax fibers.

45 However, such molding material of formaldehyde cannot have high flexural strength of more than 100 N/mm² without any filler of reinforcing fibers. If reinforcing fibers are added to formaldehyde, then the reinforcing fibers will be cut on producing the molding material and they will be oriented on molding it, which causes the mold goods to have the physical strength varied and an orientation provided thereto.

In addition thereto, since the molding material has fluidity lowered due to the filled fibers, the molding material disadvantageously fails to pervade all parts of the mold, which prevents the mold goods from having a
50 smooth surface thereof.

Conventional concrete members have been manufactured by placing freshly mixed concrete in a mold of steel, wood or FRP even though they are provided in either of factories or working spots. It will be noted that they may be advantageously manufactured by using permanent molds of precast concrete because such permanent molds are integral to the concrete members and not required to be removed. If the permanent mold
55 are formed of concrete having high durability, then the entire concrete members will have durability improved. The concrete members may have reinforcing bars used therein.

However, conventional concrete placed in the mold of steel, wood or FRP has poor wear resistance and

water tightness. Furthermore, the concrete members will have durability lowered due to rust of the reinforcing bars which is caused by chloride permeating the concrete members through fine crack or honeycomb therein which is in turn produced due to poor operation of the concrete construction or poor curing of concrete material therefor.

5 Although the property of concrete itself may be improved by adding admixtures such as fibers or silica fumes to concrete material, such improvement on the entire concrete members is undesirably expensive.

Although the entire concrete members are able to have their durability improved if the permanent molds of precast concrete having high durability are used therefor, they still have no flexural strength improved.

Such permanent molds of precast concrete are relatively thicker and heavier, which causes assemblies thereof to be troublesome. Of late, the concrete members are required to be relatively thinner and lighter.

10 Accordingly, it is a principal object of the invention to provide cement including composite material having higher flexural strength and more excellent water resistance and thermal resistance.

It is another object of the invention to provide cement products having higher physical strength such as flexural strength of more than 40 N/mm² and elastic modulus and more excellent thermal resistance and water resistance.

15 It is another object of the invention to provide molding material including cement component and having higher physical strength such as flexural strength of more than 50 N/mm² and preferably of more than 100 N/mm² and higher elastic modulus and more excellent thermal resistance and water resistance.

It is further object of the invention to provide an inexpensive concrete member having higher flexural strength and higher durability such as water tightness, chemical resistance and salt damage or weather resistance.

It is further object of the invention to provide a method of producing a concrete member having higher flexural strength and higher durability such as water tightness, chemical resistance and salt damage or weather resistance.

25 In accordance with one aspect of the present invention, there is provided cement including composite material comprising;

at least one kind of hydraulic cement;

and polymer precursor substantially including no water, but generating water by curing reaction.

30 In this aspect, the polymer precursor may be blended with a ratio of 10 to 60 weight parts and preferably 12 to 30 weight parts relative to 100 weight parts of the hydraulic cement.

Also, in this aspect, the polymer precursor may be formaldehyde resin precursor such as phenol resin precursor, melamine resin precursor or urea resin precursor or polyimide resin precursor.

In accordance with another aspect of the invention, there is provided cement including composite material comprising;

35 at least one kind of hydraulic cement;

polymer precursor substantially including no water, but generating water by curing reaction;

and additive.

In this aspect, the additive may be preferably polyamide such as fatty alcohol soluble polyamide or polyacrylamide.

40 In those two aspects, there may be added filler such as fiber material thereto.

In this aspect, the polymer precursor may be blended with the same ratio as aforementioned, but the blend ratio is set while the hydraulic cement has filler included.

In accordance with further aspect of the invention, there is provided cement product formed by curing cement including composite material comprising at least one kind of hydraulic cement and polymer precursor substantially including no water, but generating water by curing reaction.

45 In this aspect, the polymer precursor may be blended with the same ratio as aforementioned and may be added with additive and/or filler.

In accordance with further aspect of the invention, there is provided molding material comprising composite including;

50 at least one kind of hydraulic cement;

and polymer precursor substantially including no water, but generating water by curing reaction.

In this aspect, the polymer precursor may be blended with a ratio of 5 to 100 weight parts and preferably 7 to 60 weight parts relative to 100 weight parts of the hydraulic cement.

55 Also, in this aspect, the polymer precursor may be most preferably formaldehyde resin precursor such as phenol resin precursor, melamine resin precursor or urea resin precursor, but may be polyimide precursor. It should be noted that the blend ratio of polymer precursor is set while it has no alcohol solvent included.

In accordance with further aspect of the invention, there is provided a method of producing molding material comprising the step of mixing composite including at least one kind of hydraulic cement and polymer pre-

cursor substantially including no water, but generating water by curing reaction, said composite being in the form of powder.

In accordance with further aspect of the invention, there is provided a method of producing molding material comprising the step of mixing composite including at least one kind of hydraulic cement and polymer precursor substantially including no water, but generating water by curing reaction, said polymer precursor being
5 in the thermal molten form.

In accordance with further aspect of the invention, there is provided a method of producing molding material comprising the step of mixing composite including at least one kind of hydraulic cement and polymer precursor substantially including no water, but generating water by curing reaction, said polymer precursor being
10 in the thermal molten form and said composite being ground and classified.

In accordance with further aspect of the invention, there is provided a method of producing molding material comprising the step of mixing composite including at least one kind of hydraulic cement and polymer precursor substantially including no water, but generating water by curing reaction, said polymer precursor being in the form of alcohol solution of said polymer precursor.

In accordance with further aspect of the invention, there is provided a method of producing molding material comprising the step of mixing composite including at least one kind of hydraulic cement and polymer precursor substantially including no water, but generating water by curing reaction, said polymer precursor being in the form of alcohol solution of said polymer precursor and said composite being ground and classified after said alcohol is evaporated.

In these aspects of producing molding material, the polymer precursor may be blended with a ratio of 5 to 100 weight parts and preferably 7 to 60 weight parts relative to 100 weight parts of the hydraulic cement.

Also, in these aspects, the polymer precursor may be most preferably formaldehyde resin precursor such as phenol resin precursor, melamine resin precursor or urea resin precursor, but may be polyimide precursor. It should be noted that the blend ratio of polymer precursor is set while it has no alcohol solvent included.

In accordance with another aspect of the invention, there are provided mold goods obtained by molding, heating and curing molding material comprising composite including at least one kind of hydraulic cement and polymer precursor substantially including no water, but generating water by curing reaction.

In this aspect, the composite may be in the form of powder. It may be in the thermally molten form of polymer precursor or in the thermally molten form of polymer precursor and ground and classified.

Otherwise, it may be in the form of alcohol solution of said polymer precursor or in the form of alcohol solution of polymer precursor and ground and classified.

Also, in this aspect, the polymer precursor may be blended with a ratio of 5 to 100 weight parts and preferably 7 to 60 weight parts relative to 100 weight parts of the hydraulic cement.

Furthermore, in this aspect, the polymer precursor may be most preferably formaldehyde resin precursor such as phenol resin precursor, melamine resin precursor or urea resin precursor, but may be polyimide precursor. It should be noted that the blend ratio of polymer precursor is set while it has no alcohol solvent included.

In accordance with another aspect of the invention, there is provided a concrete member comprising a concrete body and at least one reinforcing body integrally provided with said concrete body, said reinforcing body comprising composite including at least one kind of hydraulic cement and polymer precursor substantially including no water, but generating water by curing reaction.
40

In this aspect, the reinforcing body may be attached to the concrete body or buried in the concrete body.

Also, in this aspect, the polymer precursor may be blended with a ratio of 5 to 100 weight parts relative to 100 weight parts of the hydraulic cement.

Furthermore, in this aspect, the polymer precursor may be most preferably formaldehyde resin precursor such as phenol resin precursor, melamine resin precursor or urea resin precursor, but may be polyimide precursor. It should be noted that the blend ratio of polymer precursor is set while it has no alcohol solvent included.

In accordance with further aspect of the invention, there is provided a method of producing a concrete member comprising the steps of;

forming at least one reinforcing body comprising composite including at least one kind of hydraulic cement and polymer precursor substantially including no water, but generating water by curing reaction;
50 placing said reinforcing body in a mold;

and placing and curing freshly mixed concrete in said mold to form said concrete member with said reinforcing body integrally provided.

In accordance with further aspect of the invention, there is provided a method of producing a concrete member comprising the steps of;

forming at least one reinforcing body comprising composite including at least one kind of hydraulic cement and polymer precursor substantially including no water, but generating water by curing reaction;
assembling a permanent mold of said reinforcing body;

and placing and curing freshly mixed concrete in said permanent mold to form said concrete member with said reinforcing body integrally provided.

In accordance with further aspect of the invention, there is provided a method of producing a concrete member comprising the steps of;

5 forming a concrete body;

forming at least one reinforcing body comprising composite including at least one kind of hydraulic cement and polymer precursor substantially including no water, but generating water by curing reaction;

adhering said reinforcing body to said concrete body by adhesive to form said concrete member.

10 In these aspects of producing a concrete member, the polymer precursor may be blended with a ratio of 5 to 100 weight parts relative to 100 weight parts of the hydraulic cement.

Furthermore, in these aspects, the polymer precursor may be most preferably formaldehyde resin precursor such as phenol resin precursor, melamine resin precursor or urea resin precursor, but may be polyimide precursor.

15 The above and other objects and features of the invention will be apparent from the description of the embodiments of the invention taken along without or with the accompanying drawings in which;

Fig. 1 is a perspective view of a concrete member constructed in accordance with one embodiment of the invention;

Fig. 2 is a cross sectional view of a concrete member together with a mold in which the concrete member is formed in accordance with one method of the invention;

20 Fig. 3 is a cross sectional view of a concrete member constructed in accordance with another embodiment of the invention;

Fig. 4 is a cross sectional view of a concrete member together with a permanent mold in which the concrete member is integrally formed in accordance with another method of the invention;

25 and Fig. 5 is a cross sectional view of a concrete member together with a mold in which the concrete member is formed in accordance with further method of the invention.

As aforementioned, the invention provides cement including composite material comprising at least one kind of hydraulic cement and polymer precursor substantially including no water, but generating water by curing reaction.

30 As the cement including composite material comprises polymer precursor substantially including no water, but generating water by curing reaction, water generated by curing reaction hydrates with hydraulic cement. This causes higher physical strength such as flexural strength and more excellent water resistance and thermal resistance to be provided to the composite material.

35 Hydraulic cement used in the invention may be of conventional cement such as Portland cement (normal Portland cement, high early strength Portland cement or moderate Portland cement, for example), blended cement (Portland blast furnace cement, silica cement or fly-ash cement, for example), special cement (aluminous cement or oil well cement, for example) and various gypsum. One or more than two kinds of hydraulic cement can be used.

Polymer precursor cured while generating water may be suitably formaldehyde resin precursor or polyimide precursor. The precursor may have predetermined viscosity adjusted by solvent in view of molding thereafter.

40 Formaldehyde precursor may be of phenol resin precursor, melamine resin precursor or urea resin precursor preferably in the form of alcohol solution with nonvolatile component of 40 to 70 % included. Alcohol which may be used in this invention is methanol, ethanol, propanol, butanol, cyclohexanol, phenol, cresol, ethylene glycol, trimethylene glycol or the like.

45 Polyimide precursor may be preferably in the form of solution for which solvent of N-methyl-2-pyrrolidone or N,N-dimethyl acetamide or the like is used and with nonvolatile component of 10 to 30 % included therein.

Polymer precursor in the form of solution and hydraulic cement are blended with a blending ratio of 10 to 60 weight parts of polymer precursor to 100 weight parts of hydraulic cement. Preferable blend ratio is of 12 to 30 weight parts of polymer precursor. If hydraulic cement has filler added, then the blend ratio of polymer precursor is to 100 weight parts of powder components of hydraulic cement having the filler added.

50 If the blend ratio of polymer precursor is less than 8 weight parts, then it will not be able to be positively blended with hydraulic cement. This also causes the resultant product to have lower physical strength.

If the blend ratio of polymer precursor is more than 60 weight parts, the resultant product has crack found and physical strength increasing not so much. Therefore, it will be noted that more than 60 weight parts of polymer precursor is not economical.

55 There may be blended additive or filler with composite material of polymer precursor and hydraulic cement, if necessary. Such additive or filler may be blended by a conventional mixer such as an Eirich type mixer or a herical mixer. If the blend ratio of polymer precursor is relatively smaller, it may be preferably blended by a mixer such as provides compression function, shearing function or spatula touching function thereto. Such a mixer

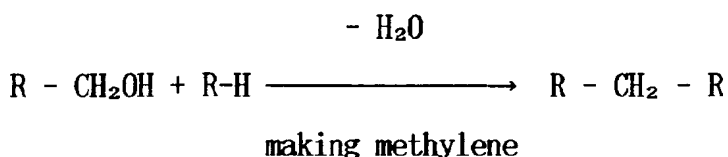
may be a kneader, a wet pan mill, a helical rotor, a roller mill, a Banbury type mixer or the like.

The kneaded cement composite material is molded by roller molding, extruder molding, press molding or pouring molding, after which polymer precursor of the cement composite material is heated and cured to form a cement product having predetermined configuration and size.

Composite material including formaldehyde precursor may be heated at a temperature of 100 to 300 °C and preferably at a temperature of 150 to 250 °C. Composite material including polyimide precursor may be heated at a temperature of 300 to 500 °C and preferably at a temperature of 350 to 450 °C. Heating composite material cures polymer precursor and generates water, whereby hydraulic cement hydrates so that the cement product has higher physical strength.

In general, formaldehyde precursor is rapidly cured in an acid area of less than pH 7, but it will be able to be fully cured even in an alkali area of more than pH 7 if it is heated at a temperature of 150 to 250 °C for a relatively longer time.

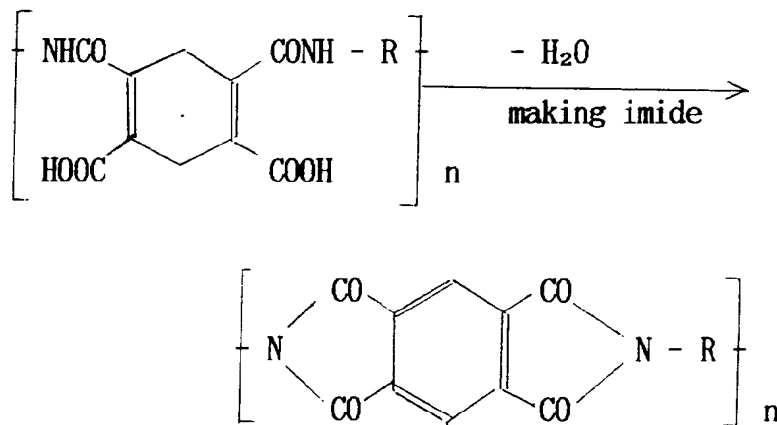
It is known that such curing reaction of formaldehyde precursor is made mainly by the following model condensation reaction;



The thus generated water hydrates hydraulic cement under heat to produce a cement hydrate.

It is known that polyimide precursor is made insoluble and infusible solid of more excellent thermal resistance when it is heated at a temperature of more than 300°C through intramolecular cyclodehydration reaction.

An example of typical curing reaction of polyimide precursor produces polyimide of more excellent thermal resistance in accordance with intramolecular cyclodehydration reaction of polyamic acid having pyrromerit acid skelton as follows;



Water generated by imide reaction of polyimide precursor hydrates hydraulic cement under heat in the same manner as water generated by curing reaction of formaldehyde precursor to produce a cement hydrate.

A cement product has texture formed by rigid three-dimensional bridge structure of formaldehyde resin or polyimide and cement hydrate involved with each other, which causes the product to have higher physical strength.

Cement composite material formed in the aforementioned manner have higher flexural strength provided thereto by heating, but it has been found that some of the cement products of the invention has higher physical strength provided thereto by immersing it in water after it is cured by heating.

Although cement composite material of the invention has no water particularly required on kneading, it may be blended with small quantity of water in consideration of premolding. Furthermore, there is added thereto additive such as glycerol, glycerol triacetate, polyethylene glycol, furfural, dibutyl phthalate, phthalic anhydride, stearic acid, rosin, polyamide, polyacrylamide, polyvinyl alcohol or the like.

Particularly, polyamide, polyacrylamide or polyvinyl alcohol is preferable additive for improvement of the cement product. The additive may be added directly to polymer precursor and then dissolved or dispersed therein, but it may be dissolved or dispersed in solvent such as ethanol, methanol or N,N-dimethylacetamide and then added to polymer precursor.

5 A blend ratio of the additive may be generally of 0.5 to 20 weight parts to 100 weight parts of polymer precursor and preferably 2 to 12 weight parts thereto.

Polyamide used in the invention may be preferably alcohol-soluble. Such alcohol-soluble polyamide may be of amide bonding - CONH - having at least a part of hydrogen substituted by methoxymethyl group or of amide bonding - CON(R) - produced from secondary amine. It will be considered that such polyamide added
10 to polymer precursor will be able to react with polymer precursor during heating and curing it in the manner corresponding to the manner in which formaldehyde resin precursor or polyimide precursor is reacted through intramolecular cyclodehydration under heat.

Furthermore, cement composite material of the invention may be blended with filler when kneaded, if necessary. A blend ratio of filler may be determined in view of formability of composite material and physical strength of the obtained product. Filler may be of conventional sand, light-weight aggregate, wood flour, ground calcium carbonate, aluminium hydroxide which may be used as incombustible agent for plastic or rubber, in-
15 organic pigment or the like.

In order to further improve the physical strength of the cement products of the invention, there may be used hydraulic cement having particle size distribution adjusted in multiple mode or hot press curing the cement products under pressure to adjust blow-holes thereof.
20

In order to improve adhesion of filler and/or hydraulic cement to resin, there may be added conventional silane coupling agent thereto. Such silane coupling agent may be of γ -aminopropyl triethoxysilane, γ -ureido-propyl triethoxysilane or γ -glycidoxypopyl trimethoxysilane.

Some examples of the invention and some comparisons will be described hereinafter.

25

EXAMPLES 1 to 3

There were kneaded 100 weight parts of hydraulic cement which was formed of normal Portland cement, alumina cement (trade name DENKA Alumina Cement No. 1 manufactured by Denki Kagaku Kogyo Kabushiki
30 Kaisya, Japan) or blend thereof, 23 weight parts of alcohol-soluble phenol resin precursor (trade name Shonol manufactured by Showa Highpolymer Co., Ltd., Japan) and 2.3 weight parts of glycerol in a mortar mixer for 6 minutes. The thus kneaded mixture passes through a pair of rollers used as a knoodle maker and having a revolution ratio identical to each other about 20 times and to form a sheet-like strip of 1.5 mm thickness, which was divided into sheet-like articles of about 25 mm width and 75 mm length. 10 sheet-like products were heated
35 and cured at a temperature of 150°C for 18 hours to make cement products.

5 cement products thereof were provided directly for bending tests while remaining 5 cement products were provided for bending tests after they were immersed in water of 20°C for three days. The bending tests were made in accordance with JIS (Japanese Industrial Standard) R 5021 with a distance of 50 mm between supporting points where the cement products were supported. Table I shows the results of the bending tests. The
40 flexural strengths of the cement products were measured immediately after they were heated at a temperature of 150°C (referred to as direct test in Table I) and after they were immersed in water thereafter.

45

50

55

Table I

| | Ex 1 | Ex 2 | Ex 3 |
|--|-------------|------|------|
| | COMPOSITION | | |
| normal Portland cement | 100 | 60 | 0 |
| alumina cement | 0 | 40 | 100 |
| phenol resin precursor | 23 | 23 | 23 |
| glycerol | 2.3 | 2.3 | 2.3 |
| flexural strength (Kgf/cm ²) | | | |
| direct test | 466 | 545 | 572 |
| after immersion in water | 460 | 581 | 599 |

EXAMPLE 4

There were kneaded 100 weight parts of alumina cement (tradename DENKA Alumina Cement No. 1 manufactured by Denki Kagaku Kogyo Kabushiki Kaisya, Japan) or blend thereof, 15 weight parts of alcohol-soluble phenol resin precursor (tradename Shonol manufactured by Showa Highpolymer Co., Ltd., Japan) and 1.5 weight parts of glycerol in a bench type kneader for 6 minutes. The thus kneaded mixture was molded in a pushing mold under pressure of 150 kgf/cm² to form cement products of 10 mm thickness, 40 mm width and 160 mm length. The cement products were heated and cured at a temperature of 150°C for 18 hours to make cement products.

5 cement products thereof were provided directly for bending tests. The bending tests were made in accordance with JIS R 5021 with a distance of 100 mm between supporting points where the cement products were supported. The resultant flexural strengths of them were 529 kgf/cm².

EXAMPLE 5

The same materials as in Example 4 were used. 100 weight parts of alumina cement, 20 weight parts of alcohol-soluble phenol resin precursor and 1.8 weight parts of glycerol were kneaded in a bench type kneader for 6 minutes. The thus kneaded mixture was molded in a vacuum extruding molding machine to form cement products of 15 mm thickness, 20 mm width and 160 mm length. The cement products were cured and provided for bending tests in the same manner as in EXAMPLE 4. The resultant flexural strengths of them were 551 kgf/cm².

EXAMPLES 6 to 10

Cement products were manufactured in the same manner as in Examples 1 to 3 except for fillers of N-methoxymethyl-polyamide having hydrogen of amido bonding substituted by methoxymethyl group by about 30 % (tradename Toresin manufactured by Teikoku Chemical Industries Co., Ltd., Japan) and ethanol additionally used and blend ratios thereof set as indicated in Table II. The cement products were provided for bending tests in the same manner as in Examples 1 to 3. The results of the tests were Table II.

Table II

| | Ex 6 | Ex 7 | Ex 8 | Ex 9 | Ex10 |
|--|-------------|------|------|------|------|
| | COMPOSITION | | | | |
| normal Portland cement | 100 | 40 | 40 | 0 | 0 |
| alumina cement | 0 | 60 | 60 | 100 | 100 |
| phenol resin precursor | 21.6 | 23 | 20 | 21.6 | 13.6 |
| polyamide | 1.4 | 0.8 | 0.8 | 1.4 | 1.4 |
| ethanol | 0 | 0 | 3.2 | 0 | 8.0 |
| glycerol | 2.3 | 2.3 | 2.0 | 2.3 | 2.3 |
| flexural strength (Kgf/cm ²) | | | | | |
| direct test | 584 | 713 | 628 | 762 | 357 |
| after immersion in water | 561 | 720 | 640 | 785 | 378 |

EXAMPLES 11 to 13

Cement products were manufactured in the same manner as in Examples 1 to 3 except for fillers of polyacryl amide (tradename Acoflock N100S manufactured by Mitsui Sianamidido Co., Ltd., Japan) or polyvinylalcohol (tradename Gosenol manufactured by Nippon Gosei Kagaku Kogyo Kabushiki Kaisya, Japan) in addition to N-methoxymethyl-polyamide (tradename Toresin manufactured by Teikoku Kagaku Kogyo Kabushiki Kaisya, Japan) of Examples 6 to 10 additionally used and blend ratios thereof set as indicated in Table III. The cement products were provided for bending tests in accordance with JIS R 5021 with a distance of 50 mm between supporting points where the cement products were supported. The results of the tests were Table III.

Table III

| | Ex 11 | Ex 12 | Ex 13 |
|--|-------------|-------|-------|
| | COMPOSITION | | |
| alumina cement | 100 | 100 | 100 |
| phenol resin precursor | 21.6 | 21.6 | 21.6 |
| polyamide | 1.4 | - | - |
| polyacrylamide | - | 1.4 | - |
| polyvinylalcohol | - | - | 1.4 |
| glycerol | 2.3 | 2.3 | 2.3 |
| flexural strength (Kgf/cm ²) | | | |
| direct test | 1160 | 1320 | 650 |

EXAMPLE 14

There were kneaded 100 weight parts of alumina cement (tradename DENKA Alumina Cement No. 1 manufactured by Denki Kagaku Kogyo Kabushiki Kaisya, Japan) and 20 weight parts of polyimide precursor (tradename U-varnish-A manufactured by Ube Kosan Co., Ltd., Japan) and molded in the same manner as in Examples 1 to 3. The thus kneaded mixture was heated and cured at a temperature of 120 °C for one hour, at 150 °C for 20 minutes, at 200 °C for 20 minutes, at 250 °C for 20 minutes and finally at 350°C for one hour to

form cement products.

The cement products were provided directly for bending tests. The bending tests were made in accordance with JIS R 5021 with a distance of 50 mm between supporting points where the cement products were supported. The resultant flexural strengths of them were 402 kgf/cm².

EXAMPLES 15 to 18

The cement products obtained in the same manner as in Examples 6 and 9 were heated at a temperature of 200°C for 18 hours or at 300 °C for 6 hours.

The cement products were provided for bending tests in the same manner as in Examples 1 to 3. In the tests, the flexural strengths of the cement products were measured before heated, after heated and after immersed in water in order to compare them. The results of the tests are indicated in Table IV.

Table IV

| | Ex 15 | Ex 16 | Ex 17 | Ex 18 |
|--|------------------------|-------|----------------|-------|
| kind of cement | normal Portland cement | | alumina cement | |
| heating temp. (°C) | 200 | 300 | 200 | 300 |
| flexural strenght (kgf/cm ²) | | | | |
| before heated | 584 | 584 | 762 | 762 |
| after heated | 713 | 792 | 1040 | 1120 |
| after immersed in water | 706 | 785 | 1060 | 1220 |

COMPOMPARISONS 1 and 2

The cement products of about 4 mm thickness having high flexural strength commercially available from a certain Japanese Company were divided into 9 pieces, three of which were provided for bending tests.

In order to determine thermal resistance of the cement products, each three remaining pieces were heated at a temperature of 200 °C for 18 hours and at a temperature of 300 °C for 6 hours, respectively and then provided for bending tests.

The bending tests were made in accordance with JIS R 5021 with a distance of 50 mm between supporting points where the cement products were supported. The results of the bending tests were indicated in Table V.

Table V

| | COMPARISON 1 | COMPARISON 2 |
|--|--------------|--------------|
| heating temp. (°C) | 200 | 300 |
| flexural strength (kgf/cm ²) | | |
| before heated | 1390 | 1390 |
| After heated | 462 | 330 |

It will be noted that the cement products of Examples 1 to 18 of the invention had higher flexural strength and more excellent thermal resistance and water resistance in comparison with the cement products of Comparisons 1 and 2.

Molding Material

This invention further provides molding material including mixture of composite material comprising at least one kind of hydraulic cement, polymer precursors substantially including no water, but generating water by curing reaction and additives and/or fillers, if necessary. The molding material has no water substantially added there-

to.

The molding material of the invention has flexural strength of more than 50 N/mm² and in some examples has flexural strength of more than 100 N/mm² even though it has no reinforcing fibers filled therein.

The molding material may be produced by mixing the composite material in the thermally molten form and thereafter grinding and classifying the same.

Otherwise, the molding material may be produced by mixing the composite material in the form of alcohol solution of the polymer precursor and thereafter grinding and classifying it without or with alcohol evaporated.

Polymer precursor used may be preferably formaldehyde resin precursor, but it may be polyimide precursor. Formaldehyde precursor may be of phenol resin precursor, melamine resin precursor or urea resin precursor, which substantially includes no water, but generates water by heating and curing. This means that the precursor potentially includes water. In this invention, "Substantially including no water means that water content of the polymer precursor is less than 5 %, preferably less than 4 % and most preferably less than 2 % relative to the weight of hydraulic cement. The water content may be measured by Karl-Fischer Method (Analytical Chemistry Manual issued by Association of Japan Analytical Chemistry in 1971, pages 31 and 32). If the water content of the polymer precursor exceeds 5 %, then hydraulic cement will be cured or weathered on manufacturing or storing the molding material, which causes the physical strength of the mold goods to be lowered.

Hydraulic cement to be used in the molding material of the invention may be of conventional cement such as Portland cement, blended cement, special cement and various gypsum which may be identical to those used in the cement composite material of the invention aforementioned. One or more than two kinds of hydraulic cement can be used. The hydraulic cement may be used as the commercially available one is, but it has particle distribution adjusted in multi mode or particle configuration rounded in order to improve the physical strength or fluidity of the molding material.

Formaldehyde precursor used in the molding material of the invention may be blended with hydraulic cement in accordance with moldability and property of the mold goods. In general, a blend ratio of formaldehyde precursor may be 5 to 100 weight parts and preferably 7 to 60 weight parts to 100 weight parts of hydraulic cement. If the blend ratio of formaldehyde precursor is less than 5 weight parts, then the blended condition of the components and the fluidity of the molding material is lowered and the mold goods have defect produced therein. If it is more than 100 weight parts, then the mold goods disadvantageously have cracks found therein and physical strength heightened no longer or otherwise lowered. The blend ratio of formaldehyde resin precursor is set while it has no alcohol included therein.

There may be preferably blended the molding material of the invention with additive of polymer having acid amide bonding such as polyamide or polyacryl, for example, in order to improve property of the mold goods.

In general, a blend ratio of the additive may be 0.5 to 30 weight parts and preferably 2 to 20 weight parts relative to 100 weight parts of formaldehyde precursor. If it is less than 0.5 weight parts, then there appears no improvement on property of the mold goods. Also, if it is more than 30 weight parts, there ineconomically increases no improvement on property of the mold goods.

The additive may be preferably finely ground before blended. When it is to be blended using alcohol, polyamide may be preferably alcohol-soluble. Such alcohol-soluble polyamide may be amide bonding - CONH - having at least a part of hydrogen substituted by methoxymethyl group or of amide bonding - CON(R) - produced from secondary amine.

The molding material of the invention may be blended with other additive such as conventional lubricant, silane coupling agent or coloring agent in addition to the aforementioned polyamide. Lubricant may be formed of glycerol, glycerol triacetate, phthalic anhydride, furfural, alkyl phenol, zinc stearate, magnesium stearate, rosin or the like. Silane coupling agent may be of γ -aminopropyl triethoxysilane, γ -ureidopropyl triethoxysilane or γ -glycidopropyl triethoxysilane. Coloring agent may be formed of organic or inorganic pigment such as aniline black, carbon black or titanium oxide.

Furthermore, molding material of the invention may be blended with filler. Such filler may be of conventional one such as wood flour, pulp, cotton flock, stone dust, ground calcium carbonate, aluminium hydroxide, sand, light-weight aggregate, glass fibers, carbon fibers or the like. Polymer precursor may have the blend ratio thereof increasing as the amount of the filler increases.

A method for manufacturing molding material of the invention will be described hereinafter.

Formaldehyde precursor, hydraulic cement and additive are blended so as to uniformly disperse their components to form the molding material of the invention. They may be blended by a conventional mixing machine such as a mortar mixer, a kneader, a blender or a roller machine. The proper mixing machine may be preferably selected in accordance with the blend ratio of the components and a mixing system described hereinjust below.

A first mixing system is one in which the components in the form of powder may be mixed at the normal

temperature by a conventional cold mixing machine such as a kneader, a mortar mixer or a blender. The components may be preferably finely ground or may be preferably dispersed in a small quantity of solvent such as methanol or ethanol which is added thereto in order to effectively prevent them from being scattered. The mixture in the form of powder may be dried, if necessary, to obtain the molding material.

5 A second mixing system is one in which the components in the thermally molten form may be thermally mixed by a conventional thermal mixing machine such as a Banbury type mixer, a kneader or a hot roller machine, which is heated by a steam heater or an electric heater. A temperature at which the components are heated is so set that formaldehyde precursor is fully molten, but a reaction in which it is made methylene does not progress so much. In general, the preferable temperature is 80 to 150°C. If it exceeds 150 °C, formaldehyde precursor is cured too much before the components are fully mixed.

10 The mixture which is obtained by thermally mixing the components is dried, ground and classified to form the molding material. Otherwise, the mixture which is obtained by thermally mixing the components is used as the molding material without grinding and classifying it in view of a molding method and/or a product configuration in manufacturing the mold goods.

15 A third mixing system is one in which the components in the form of alcohol solution of formaldehyde precursor may be mixed by a conventional mixing machine such as a kneader, a Banbury type mixer, a mortar mixer or a two-roller machine.

In general, this mixing is made at the normal temperature, but it may be made while alcohol is heated nearly at its boiling temperature in order to enhance an evaporation of alcohol if the components are fully dispersed in alcohol.

20 Formaldehyde precursor used for the molding material is alcohol-soluble and it is used in the form of alcohol solution. A quantity of alcohol used therefor may be determined in view of the dispersion effect of the components and moldability of the molding material. Preferably, it may be alcohol solution having 20 to 80 % of nonvolatile component included therein.

25 Alcohol which is used in the molding material of this invention may be methanol, ethanol, propanol, butanol, cyclohexanol, phenol, cresol, ethylene glycol, trimethylene glycol or the like.

The mixture which is obtained by mixing the components is dried to evaporate alcohol, if necessary, and thereafter ground and classified to form the molding material. Otherwise, the mixture which is obtained by mixing the components is used as the molding material without grinding and classifying it in view of a molding method and/or a product configuration in manufacturing the mold goods.

30 The thus obtained molding material may be molded by compression molding, transfer molding, injection molding, extrusion molding, flowing-in molding (pouring molding) or the like and heated while or after molded to form the mold goods. A heating temperature may be 100 to 300 °C and preferably 150 to 250 °C. This heating is considered to cure formaldehyde resin precursor and generates water, which causes hydraulic cement to hydrate to provide higher physical strength thereto. It is considered that this higher physical strength will be brought by aluminium ion ion-bridging with resin which is caused by a small quantity of water generated therein.

35 Although, in the aforementioned, formaldehyde resin precursor is used as polymer precursor, it should be understood that polyimide precursor may be used as polymer precursor.

40 The mold goods manufactured by the invention may be applied for various uses. They may be used for transportation fields such as bodies, ship parts, pallets or the likes, electronic or electric fields such as instrument housings, insulation parts, IC sealers, parabola antennas, printed circuit board, a floor for office automation device or the likes, public engineering or construction fields such as concrete reinforcing materials, concrete molds, composite molds such as superstrong composite molds, paving materials, tiles, water tanks, roofing materials (roofing tile, roofing slate and others), inner or outer wall materials, ceiling materials, partition wall materials, column for road, capsule houses, light-weight manhole, artificial marble products such as kitchen counters or washing stands or the likes, chemical industry fields such as tanks, pipes, pipe covering or the likes and general machine fields such as gears or the likes.

45 Some examples of the molding materials of the invention and one comparison will be described hereinafter.

50 EXAMPLES 19 and 20

55 There were blended and mixed alumina cement (tradename DENKA Alumina Cement No. 1 manufactured by Denki Kagaku Kogyo Kabushiki Kaisha, Japan), phenol resin precursor (tradename Shonol BRG-558 manufactured by Showa Highpolymer Co., Ltd., Japan), hexamethylene tetramine, zinc stearate, furfural and coloring agent (tradename BAYERTITAN manufactured by Bayer Japan Co., Ltd., Japan) by a roller mill for rubber which was heated at a temperature of 110 °C by steam. A revolution ratio of rollers was set at 1 to 1.3. The water content of phenol resin precursor measured by Karl-Fischer method was 0.1 %.

Dough mixture which was wound on the rollers of the roller mill was removed out of the rollers and thereafter ground in a stainless steel mortar to form the molding material. The molding material was filled in a die having 120 °C maintained and compressively molded under 10 N/mm². Thereafter, the die temperature was raised to 180°C and maintained at this temperature for 6 hours °C to form sheet-like mold goods of about 3 mm thickness.

The sheet-like mold good was divided into 10 pieces of 15 mm width and 80 mm length. 5 pieces thereof were provided directly for bending tests while remaining 5 pieces were provided for bending tests after they were immersed in water of 20 °C for seven days. The bending tests were made by a bisecting point loading method with a distance of 60 mm between supporting points where the pieces were supported. Flexural elastic modulus was determined by measuring flexure at the middle of the tested pieces.

The composition of Examples 19 and 20 are indicated at Table VI-I and the results of the tests are shown in Table VI-II.

Table VI-I

| | Ex 19 | Ex 20 | Ex 21 |
|-------------------------|----------------|----------------|-----------------|
| | Composition | | |
| alumina cement | 100 | 100 | 100 |
| phenol resin precursor | 25.0 (BRG-558) | 16.6 (BRG-558) | 22.0 (BKM-2620) |
| hexamethylene-tetramine | 2.50 | 1.66 | - |
| zinc stearate | 0.50 | 0.33 | 0.22 |
| furfural | - | 1.60 | - |
| coloring agent | 3.00 | - | - |

Table VI-II

| | Ex 19 | Ex 20 | Ex 21 |
|---------------------------|--|-------|--------------|
| | flexural strength (N/mm ²) | | |
| before immersion in water | 130 | 102 | 58.0 |
| after immersion in water | 153 | 105 | not measured |
| | flexural elastic modulus (kN/mm ²) | | |
| before immersion in water | 33.8 | 35.3 | not measured |
| after immersion in water | 33.1 | 35.1 | not measured |
| | water absorption rate after immersion in water % | | |
| | 0.19 | 0.21 | not measured |

EXAMPLES 21

There were ground in a stainless steel mortar alumina cement (tradename DENKA Alumina Cement No. 1 manufactured by Denki Kagaku Kogyo Kabushiki Kaisya, Japan) and phenol resin precursor (tradename Shonol BKM-2620 manufactured by Showa Highpolymer Co., Ltd., Japan) and added thereto zinc stearate in the form of powder in a mortar mixer for four minutes to form molding materials. The water content of phenol resin precursor measured by Karl-Fischer method was 4.5 %. The molding materials were molded to form testing pieces in the same manner as in Examples 19 and 20.

The composition of Example 21 is indicated in Table VI-I and the result of the test is shown in Table VI-II.

EXAMPLES 22 to 25

There were blended and premixed normal Portland cement, alumina cement (tradename DENKA Alumina Cement No. 1 manufactured by Denki Kagaku Kogyo Kabushiki Kaisya, Japan), phenol resin precursor (trade-
 name Shonol BRS-330 manufactured by Showa Highpolymer Co., Ltd., Japan, with 60.6 % of nonvolatile component included therein and water content of 1.3 %), polyamide including amide bonding - CONH - having at least a part of hydrogen substituted by methoxymethyl group (tradename Toresin manufactured by Teikoku Chemical Industries Co., Ltd., Japan), glycerol and silane coupling agent (tradename KBE-903 manufactured by Shin-Etsu Chemical Co., Ltd., Japan) in a mortar mixer for two minutes. Thereafter, they were mixed for four minutes in a roller mill for rubber having a revolution ratio of a pair of rollers of 1 to 1.2.

Dough mixture which was wound on the rollers of the roller mill was removed out of the rollers to form sheet-like molding materials of about 2 mm thickness. The sheet-like molding materials were compressively molded in a die of 80 °C under compression stress of 6 N/mm² and heated at a temperature of 200°C for 15 hours to form sheet-like molded goods.

The sheet-like mold good was divided into 10 pieces of 25 mm width and 100 mm length, which were provided for tests identical to those in Examples 19 and 20.

The composition of Examples 19 and 20 are indicated in Table VII-I and the results of the tests are shown in Table VII-II. The tested pieces were subject to X-ray diffraction in which there were found no peak in cement hydrate.

Table VII-I

| | Ex 22 | Ex 23 | Ex 24 | Ex 25 |
|------------------------|-------|-------|-------|-------|
| Composition | | | | |
| normal Portland cement | 100 | 60 | - | - |
| alumina cement | - | 40 | 100 | 100 |
| phenol resin precursor | 18.4 | 19.3 | 21.2 | 21.2 |
| polyamide | 1.6 | 1.7 | 1.8 | 1.8 |
| glycerol | 2.0 | 2.2 | 2.3 | 2.3 |
| coupling agent | - | - | - | 2.3 |

Table VII-II

| | Ex 22 | Ex 23 | Ex 24 | Ex 25 |
|--|-------|-------|-------|-------|
| flexural strength (N/mm ²) | | | | |
| before immersion in water | 104 | 165 | 191 | 204 |
| after immersion in water | 70.5 | 156 | 212 | 208 |
| flexural elastic modulus (kN/mm ²) | | | | |
| before immersion in water | 45.4 | 47.8 | 38.5 | 39.3 |
| after immersion in water | 40.7 | 44.9 | 34.5 | 35.1 |
| water absorption rate after immersion in water % | | | | |
| | 1.57 | 0.34 | 0.16 | 0.15 |

EXAMPLES 26 to 29

There were blended and mixed in addition to components in Example 23 melamine resin precursor (manufactured by Mitsui Toatsu Chemicals, Inc., Japan having 74.6 % of nonvolatile component included therein

and water content of 4.3 %) in the form of alcohol solution as formaldehyde resin precursor and polyacrylamide as additive in such composition as shown in Table VIII-I. After the components were premixed in a bench type kneader for two minutes, they were mixed for four minutes in a roller mill for rubber having a revolution ratio of a pair of rollers of 1 to 1.2 set.

Dough mixture which was wound on the rollers of the roller mill was removed out of the rollers to form sheet-like molding materials of about 3 mm thickness. The sheet-like molding materials were rolled several times through a roll mill having a revolution ratio of 1 to 1 until it has a thickness of about 1.5 mm and heated at a temperature of 200°C for 15 hours to form sheet-like mold goods. The sheet-like mold good was divided into 10 pieces of 25 mm width and 100 mm length, which were provided for tests identical to those in Examples 19 and 20.

The composition of Examples 26 to 29 are indicated in Table VIII-I and the results of the tests are shown in Table VIII-II.

Table VIII-I

| | Ex 26 | Ex 27 | Ex 28 | Ex 29 |
|--------------------------|-------|-------|-------|-------|
| Composition | | | | |
| normal Portland cement | 100 | - | - | - |
| alumina cement | - | 100 | 100 | 100 |
| phenol resin precursor | 30.0 | 21.2 | 21.2 | - |
| melamine resin precursor | - | - | - | 18.0 |
| polyamide | - | 1.6 | - | 4.0 |
| polyacrylamide | - | - | 1.6 | - |
| glycerol | 3.0 | 2.3 | 2.3 | 4.0 |

Table VIII-II

| | Ex 26 | Ex 27 | Ex 28 | Ex 29 |
|--|-------|-------|-------|--------------|
| flexural rigidity (N/mm ²) | | | | |
| before immersion in water | 71.1 | 112 | 125 | 33.5 |
| after immersion in water | 64.0 | 126 | 103 | not measured |
| flexural elastic modulus (kN/mm ²) | | | | |
| before immersion in water | 28.4 | 32.8 | 32.7 | not measured |
| after immersion in water | 27.1 | 30.5 | 28.4 | not measured |
| water absorption rate after immersion in water % | | | | |
| | 2.16 | 0.42 | 0.63 | not measured |

EXAMPLE 30 and COMPOMPARISON 3

The mold goods of Example 27 were heated at a temperature of 300°C for six hours for appreciating thermal resistance thereof and provided for bending tests. In comparison, the mold goods of about 4 mm thickness having high flexural strength commercially available from a certain Japanese Company were divided into pieces of 25 mm width and 75 mm length, which were heated at the same temperature for the same hours and provided for bending tests.

Table IX shows flexural strength of the tests.

Table IX

| | Ex 30 | COMPARISON 3 |
|--|-------|--------------|
| flexural strength (N/mm ²) | | |
| before heated | 112 | 136 |
| after heated | 106 | 32.4 |

It will be noted that the mold goods of Examples 19 to 30 had higher flexural strength, elastic modulus and more excellent thermal resistance and water resistance in comparison with the mold goods of Comparisons 3.

(Concrete Member)

Also, this invention further provides a concrete member having a concrete body and reinforcing body provided on a surface of the concrete body or in the concrete body. The reinforcing body comprising at least one kind of hydraulic cement, polymer precursor such as formaldehyde precursor or polyimide precursor substantially including no water, but generating water by curing reaction and additive and /or filler, if necessary.

The reinforcing body may be provided on or in the concrete body by various methods such as burying method or permanent mold method, which will be described in detail later.

Hydraulic cement used in the reinforcing body of the invention may be conventional cement such as Portland cement, blended cement, special cement and various gypsum which may be identical to those used in the cement composite material or molding materials of the invention described with reference to Examples 1 to 30. One or more than two kinds of hydraulic cement can be used.

Polymer precursor is preferably formaldehyde resin precursor, but it may be polyimide precursor.

Formaldehyde resin precursor used for the reinforcing body of the invention may be phenol resin precursor, melamine resin precursor or urea resin precursor, which substantially includes no water, but generates water by heating and curing.

Formaldehyde resin precursor used for the reinforcing body of the invention is alcohol-soluble and it is used in the form of alcohol solution. Alcohol which is used in the reinforcing body of this invention may be methanol, ethanol, propanol, butanol, cyclohexanol, phenol, cresol, ethylene glycol, trimethylene glycol or the like.

Formaldehyde resin precursor for the reinforcing body of the invention is blended with hydraulic cement in accordance with moldability and property of the reinforcing body. In general, a blend ratio of formaldehyde resin precursor may be 5 to 100 weight parts (excluding alcohol) to 100 weight parts of hydraulic cement. If the blend ratio of formaldehyde resin precursor is less than 5 weight parts, then the blended condition of the components will be made worse and the reinforcing body has defect produced therein. If it is more than 100 weight parts, the reinforcing body disadvantageously has cracks produced therein and physical strength heightened no longer or otherwise lowered.

There may be preferably blended the reinforcing body of the invention with additive of polymer having acid amide bonding such as polyamide or polyacryl, for example, in order to improve property of the reinforcing body.

In general, a blend ratio of the additive may be 0.5 to 30 weight parts and preferably 2 to 20 weight parts relative to 100 weight parts of formaldehyde resin precursor. If it is less than 0.5 weight parts, then there will appear no improvement on property of the reinforcing body while if it is more than 30 weight parts, there will ineconomically increase no improvement on property of the reinforcing body in the same manner as the cement including composite material and the mold goods of the invention described with respect to Examples 1 to 30.

The reinforcing body of the invention may be blended with other additive such as conventional lubricant, silane coupling agent or coloring agent in addition to the aforementioned polyamide. Lubricant may be glycerol, glycerol triacetate, phthalic anhydride, furfural, alkyl phenol, zinc stearate, magnesium stearate, rosin or the like. Silane coupling agent may be of γ -aminopropyl triethoxysilane, γ -ureidopropyl -triethoxysilane or γ -glycidoxypropyl triethoxysilane. Coloring agent may be formed of organic or inorganic pigment such as aniline black, carbon black or titanium oxide. It will be noted that these additives are identical to those used in the cement including composite materials and the molding materials of the invention with respect to Examples 1 to 30.

Furthermore, the reinforcing body of the invention may be blended with conventional filler such as wood flour, pulp, cotton flock, stone dust, ground calcium carbonate, aluminium hydroxide, sand, light-weight aggregate, glass fibers, carbon fibers or the like, which are also identical to those used in the cement including com-

posite materials and the moulding materials with respect to Examples 1 to 30.

Formaldehyde resin precursor, hydraulic cement and additive and/or filler added, if necessary, are mixed in the form of powder, paste or sheet in a mortar mixer, a blender, a kneader or a hot roller machine.

Thereafter, they are molded to a predetermined shape and heated and cured. The mixture after they are mixed is dried, ground and classified to form material for reinforcing body, which may be molded by compression molding, extrusion molding or injection molding. A heating temperature may be 100 to 300 °C and preferably 150 to 250°C.

A method for manufacturing a concrete member of the invention will be described with reference to the accompanying drawings hereinafter.

As shown in Fig. 1, a concrete member 1 constructed in accordance with one embodiment of the invention comprises a concrete body 2 and two reinforcing body 3 integrally mounted on both surfaces of the concrete body 2. It should be noted that only one reinforcing product 3 may be mounted on one of the surfaces of the concrete body 2. The reinforcing body or bodies are of such a construction as aforementioned.

As shown in Fig. 2, the reinforcing body 3 may be placed on an inner bottom of a mold 4 and freshly mixed concrete may be placed into the mold 4 and cured to form the concrete body 2 integrally provided with the reinforcing body 3.

As shown in Fig. 3, the reinforcing body 3 may be adhered by adhesive agent 5 to the surface of the concrete body 2 which is previously formed by a mold into which freshly mixed concrete is placed.

As shown in Fig. 4, the concrete body 2 may be molded in a permanent mold 6 into which freshly mixed concrete is placed. The permanent mold 6 is formed of a plate-like mold portion 7 of wood or metal and a box-like mold portion 8 of reinforcing body which may be produced in the same manner as the reinforcing body 3.

After the concrete body 2 is formed, only the plate-like mold portion 7 is removed out of the concrete body 2. The box-like mold portion 8 of reinforcing body is integrally mounted on the cured concrete body 2. In order to support the box-like mold portion 8 on the plate-like mold portion 7, there may be provided supporting members 9 which serve to prevent the box-like mold portion 8 from falling due to pressure from freshly mixed concrete being placed into the permanent mold 6.

Otherwise, as shown in Fig. 5, the reinforcing product 3 is placed in the mold 4 so that the reinforcing product 3 is spaced from the inner bottom of the mold 4 by a spacer not shown. Thus, it will be noted that the concrete body 2 has the reinforcing body 3 integrally provided therein.

The reinforcing body used for the concrete member of the invention may have no surface treatment made and integrally provided on or in the concrete body, but it may preferably have roughness provided on the surface thereof on which the concrete body is provided.

Alternately, it may have adhesive agent of epoxy resin, unsaturated polyester resin or the like provided on the surface thereof on which the concrete body is mounted or a coat layer formed on the surface thereof by coating styrene-butadiene copolymer, acrylonitrile-butadiene copolymer, ethylene-vinylacetate copolymer and the like in the form of latex or emulsion before freshly mixed concrete is placed.

Freshly mixed concrete to be placed may be normal concrete, light-weight concrete, high strength concrete, resin concrete or mortar thereof, but it is never limited to particular concrete.

Furthermore, the concrete member of the invention may have conventional reinforcing bars provided therein together with the reinforcing body of the invention.

Some examples of the concrete member of the invention will be described hereinafter.

EXAMPLE 31

There were blended and premixed 100 weight parts of alumina cement (tradename DENKA Alumina Cement No. 1 manufactured by Denki Kagaku Kogyo Kabushiki Kaisha, Japan), 21.6 weight parts of phenol resin precursor (tradename Shonol BRS-330 having nonvolatile component of 60.6 % manufactured by Showa High-polymer Co., Ltd., Japan), 1.4 weight parts of N-methylmethyl polyamide having hydrogen of amide bonding substituted by methylmethyl group by 30 % (tradename Toresin manufactured by Teikoku Chemical Industries Ltd., Japan) and 2.3 weight parts of glycerol in a mortar mixer for two minutes.

Thereafter, they were mixed in a roller mill for rubber having a revolution ratio of 1 to 1.3 set for four minutes. Dough mixture which was wound on the rollers of the roller mill was removed out of the rollers.

Thereafter, it passed several times through a roller machine having a revolution ratio of 1 to 1 set and was reduced to form a sheet-like product of 2 mm thickness, which was heated at a temperature of 200°C for 18 hours to form a reinforcing product.

As shown in Fig. 2, the reinforcing body of 2 mm thickness, 40 mm width and 160 mm length was placed in the inner bottom of the steel mold of 40 mm thickness, 40 mm width and 160 mm length and thereafter

freshly mixed normal concrete shown in Table X was placed into the steel mold.

When 24 hours lapsed after the concrete was placed, the concrete member was protected in a steam atmosphere of 65°C for four hours to produce the complete concrete member.

The concrete member having an age of 7 days was provided for bending test in accordance with JIS 5201.

5 As the result of the bending test, the flexural strength of the concrete member was 17.7 N/mm² and it was found that it was about 1.9 times of 9.5 N/mm² of conventional concrete member formed of only normal concrete produced on the same conditions.

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Table X

| (Weight Parts) | Normal concrete | Normal Mortar | Light-weight Mortar |
|---|--------------------|------------------|------------------------|
| normal Portland cement | 100 | 100 | 100 |
| water | 30 | 30 | 44 |
| naphthol high quality water reduc- tion agent | 2.5 | 2.2 | 1.0 |
| fine aggre- gate A* | 155 | 180 | - |
| fine aggre- gate B** | 130 | - | - |
| light- weight aggre- gate (pear- lite) | - | - | 32 |

* Ground sand of less than 5 mm particle diameter

** Ground stone of 5 to 10 mm particle diameter

EXAMPLE 32

Normal concrete having a size of 40 mm × 40 mm × 160 mm and composition of Table X was molded and protected and cured in a steam atmosphere of 65 °C for four hours. The normal concrete after an age of 7 days has the reinforcing body of Example 31 adhered by epoxy resin adhesive to a bottom thereof as shown in Fig. 3 to produce a concrete member. After curing the adhesive, the concrete member was provided for bending test in accordance with JIS 5201.

As the result of the bending test, the flexural strength of the concrete member was 16.4 N/mm² and it was found that it was about 1.7 times of 9.5 N/mm² of conventional concrete member formed of only normal concrete produced on the same conditions.

EXAMPLE 33

As shown in Fig. 4, a box-like mold portion formed of reinforcing body of Example 31 having 2 mm thickness, 40 mm width and 160 mm length was supported by the supporting member on the steel plate and partitioned at its end by plywood to form a permanent mold. In this permanent mold was placed normal mortar of Table X, which was protected in a steam atmosphere of 65 °C for 24 hours to produce a concrete member of 15 mm thickness, 40 mm width and 160 mm length having the reinforcing body integrally provided therewith. The concrete member after an age of 7 days was provided for bending test in accordance with JIS 5201.

As the result of the bending test, the flexural strength of the concrete member was 45.4 N/mm² and it was found that it was about 3.3 times of 13.6 N/mm² of conventional member formed of only normal mortar produced on the same conditions.

EXAMPLE 34

The concrete member was produced and tested in the same manner as in Example 32, except for light-weight mortar used as material to be placed in place of normal concrete.

As the result of the bending test, the flexural strength of the concrete member was 17.8 N/mm² and it was found that it was about 4.9 times of 3.6 N/mm² of conventional member formed of only light-weight mortar produced on the same conditions. The concrete member of Example 34 had specific gravity of 1.69, which means that it was light.

EXAMPLE 35

A concrete member was produced in the same manner as in Example 31 except for the reinforcing body placed in a steel mold as shown in Fig. 5. The reinforcing body was formed by forming therein a circular opening of 10 mm diameter (pitch of 20 mm) before being heated and thereafter being heated. The reinforcing body was supported by the spacer not shown in the steel mold of 15 mm thickness, 200 mm width and 200 mm length.

In the steel mold was placed normal mortar of Table X, which was protected in a steam atmosphere of 65 °C for four hours when 24 hours lapsed after the mortar was placed to produce the complete concrete member. The concrete member after its age of 7 days was cut into pieces of 40 mm width and 200 mm length and provided for bending tests in accordance with JIS 5201.

As the result of the bending test, the flexural strength of the concrete member was 19.7 N/mm² and it was found that it was about 1.5 times of 13.6 N/mm² of conventional concrete member formed of only mortar produced on the same conditions.

EXAMPLE 36

A concrete member of 40 mm thickness, 40 mm width and 160 mm length was produced in the same manner as in Example 31. The reinforcing body was dried at a temperature of 80°C and thereafter was coated with epoxy resin on the surface thereof except for the surface of reinforcing body. After the thus obtained concrete member was immersed in water for one month, the water absorption thereof was measured. After that, it was immersed in a solution of 5 % hydrochloric acid and the state of erosion was observed. The conventional concrete member having no reinforcing body of the invention provided therein was tested in the same manner.

As the result of the test, the water absorption of the concrete member of Example 36 was 0.5 % and the erosion of the surface thereof was not found after it was immersed in the solution of 5 % hydropholic acid. On the other hand, the conventional concrete member formed of only concrete produced on the same conditions

had water absorption of 3.4 % and the paste of the conventional member was corroded after it was immersed in a solution of 5 % hydrophobic acid. The conventional concrete member had the rough surface provided thereon.

As noted from Examples 31 to 36, the concrete member of the invention had higher flexural strength and as a result the reduced cross section and the light weight thereof were obtained. In addition thereto, it had durabilities such as water tightness, chemical resistance and weather resistance or salt damage resistance.

The concrete member of the invention can be applied to materials for a construction field such as footing, pillar, beam, floor materials, external wall materials, interior finishing material, materials for civil engineering field such as canal, bridge, paving material, tunnel, tank and railing tie, materials for machinery field such as a base for machine tool, press die or the likes.

Although some embodiments of the invention have been described and illustrated without and with reference to the accompanying drawings, it will be understood by those skilled in the art that they are by way of examples, and that various changes and modifications may be made without departing from the spirit and scope of the invention, which is defined only to the appended claims.

Claims

1. Cement including composite material comprising;
at least one kind of hydraulic cement; and characterised by a polymer precursor substantially including no water, but generating water by curing reaction.
2. Cement including composite material as set forth in claim 1, wherein said polymer precursor is blended with a ratio of 10 to 60 weight parts relative to 100 weight parts of said hydraulic cement.
3. Cement including composite material as set forth in claim 2, wherein said polymer precursor is blended with a ratio of 12 to 30 weight parts relative to 100 weight parts of said hydraulic cement.
4. Cement including composite material as set forth in any one of claims 1 to 3, wherein said polymer precursor is formaldehyde resin precursor.
5. Cement including composite material as set forth in claim 4, wherein said formaldehyde resin precursor is any one of a phenol resin precursor, a melamine precursor, or a urea resin precursor.
6. Cement including composite material as set forth in any one of claims 1 to 3, wherein said polymer precursor is polyimide precursor.
7. Cement including composite material as claimed in any one of claims 1 to 6, further including:
an additive.
8. Cement including composite material as set forth in any one of claims 1 to 7, and further including filler.
9. Cement including composite material as set forth in claim 7 or 8, wherein said additive is a polyamide.
10. Cement including composite material as set forth in claim 9, wherein said polyamide is a fatty acid alcohol soluble polyamide.
11. Cement including composite material as set forth in either of claims 7 or 8, wherein said additive is a polyacrylamide, or a polyvinylalcohol.
12. Cement including composite material as set forth in any one of claims 7 to 11, wherein said additive is blended with a ratio of 0.5 to 20 weight parts relative to 100 weight parts of said polymer precursor.
13. Cement including composite material as set forth in any one of claims 7 to 12, wherein said additive is blended with a ratio of 2 to 12 weight parts relative to 100 weight parts of said polymer precursor.
14. Cement product characterised in that it is formed by curing cement as claimed in any one of claims 1 to 13.
15. Molding material characterised by comprising the cement composite material as claimed in any one of

claims 1 to 13.

16. Molding material as set forth in claim 15, wherein said polymer precursor is blended with a ratio of 5 to 100 weight parts relative to 100 weight parts of said hydraulic cement.
- 5 17. Molding material as set forth in claim 15, wherein said polymer precursor is blended with a ratio of 7 to 60 weight parts relative to 100 weight parts of said hydraulic cement.
18. Molding material as set forth in any one of claims 15 to 17, wherein said composite is mixed in the form of powder.
- 10 19. Molding material as set forth in any one of claims 15 to 17, wherein said composite is mixed in the thermally molten form of said polymer precursor.
20. Molding material as set forth in claim 19, wherein said composite is ground and classified.
- 15 21. Molding material as set forth in any one of claims 15 to 17, wherein said composite is mixed in the form of alcohol solution of said polymer precursor.
22. Molding material as set forth in claim 21, wherein said composite with said alcohol evaporated is ground and classified.
- 20 23. Molding material as set forth in any one of claims 15 to 22, wherein said additive is a polymer having acid-amide bonding included therein.
- 25 24. A method producing molding material as claimed in any one of claims 15 to 23 comprising the step of mixing the composite and curing the composite whilst generating water by the curing reaction.
25. Mold goods obtained by molding, heating and curing molding material as claimed in any one of claims 15 to 23.
- 30 26. A concrete member comprising a concrete body (2) and at least one reinforcing body (3) integrally provided with said concrete body, said reinforcing body comprising a cement as claimed in any one of claims 1 to 14.
- 35 27. A concrete member as set forth in claim 26, wherein said reinforcing body is attached to said concrete body.
28. A concrete member as set forth in claim 26, wherein said reinforcing body is provided in said concrete body.
- 40 29. A method of producing a concrete member comprising the steps of;
forming at least one reinforcing body comprising a cement as claimed in any one of claims 1 to 14;
placing said reinforcing body in a mold (4; 5);
and placing and curing freshly mixed concrete in said mold to form said concrete member.

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FIG. 1

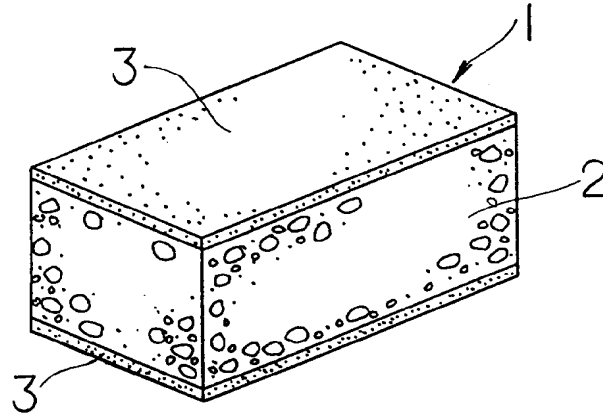


FIG. 2

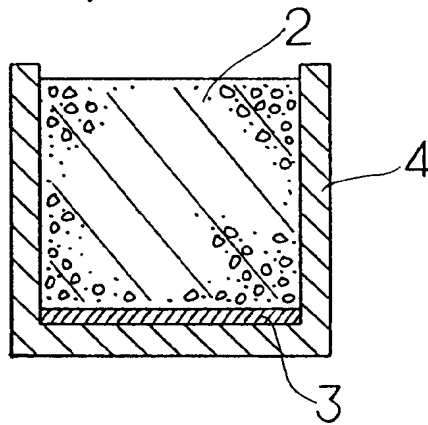


FIG. 3

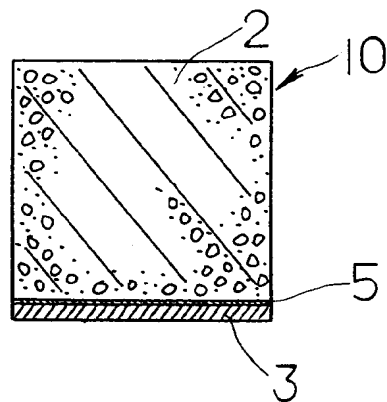


FIG. 4

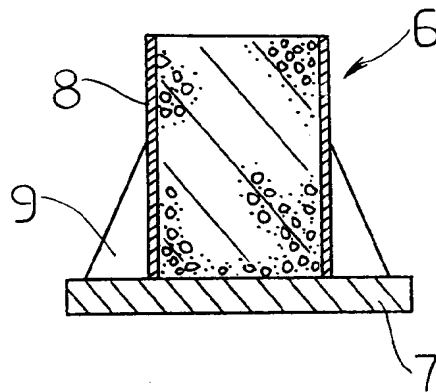
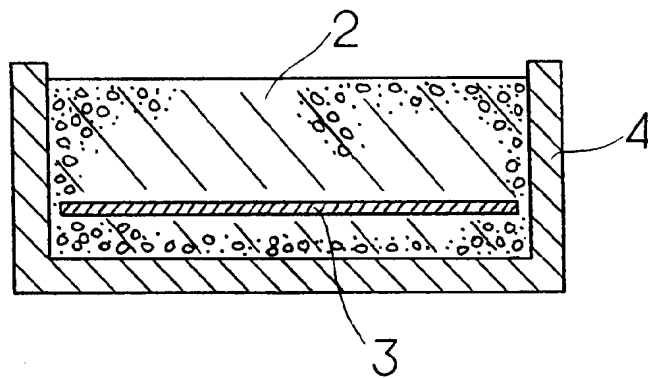


FIG. 5





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 30 7706

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
|--|--|---|--|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int.Cl.5) |
| X | GB-A-260 653 (A.H. BROWN ET AL.) * page 3, line 87 - line 93 * * page 3, line 87 - line 93 * * page 4, line 4 - line 24 * * page 5, line 9 - line 17 * | 1,4,5,7, 8,14-19, 21,24,25 | C04B40/00 C04B24/28 C04B28/02 E04C5/07 E04C3/29 B28B7/34 //(C04B28/02, 24:26,24:28) |
| Y | --- | 26-29 | |
| Y | DE-A-31 05 459 (K. VISSER) * abstract * * figure 1 * | 26,27 | |
| Y | --- | | |
| Y | FR-A-1 296 929 (L.I.VIERA RIOS) * claim 1A * | 28,29 | |
| A | --- | | |
| A | US-A-2 328 290 (H. NIEDERREITHER ET AL.) * page 1, left column, line 19 - line 28 * * page 4, left column, line 23 - line 38 * * claim 1 * | 1,15,18, 21,22 | |
| | | | TECHNICAL FIELDS SEARCHED (Int.Cl.5) |
| A | US-A-3 677 994 (H.V. WOOD ET AL.) * abstract * * column 2, line 54 - column 3, line 16 * * column 4, line 1 - line 5 * | 1-3 | C04B E04C B28B |
| A | --- | | |
| A | FR-A-2 354 866 (K. K. KROYER) * claims 1,12 * | | |
| A | --- | | |
| A | FR-A-721 548 (CELLON-WERKE) * page 3, line 15 - line 20; claim 1 * | | |
| The present search report has been drawn up for all claims | | | |
| Place of search THE HAGUE | | Date of completion of the search 7 December 1993 | Examiner Daeleman, P |
| CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document | | T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document | |

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